

Extension of the PS-GVB Electronic Structure Code to Transition Metal Complexes

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ABSTRACT: We have developed a parameterization enabling *ab initio* electronic structure calculation via the PS-GVB program on transition-metal-containing systems using two standard effective core potential basis sets. Results are compared with Gaussian-92 for a wide range of complexes, and superior performance is demonstrated with regard to computational efficiency for single-point energies and geometry optimization. Additionally, the initial guess strategy in PS-GVB is shown to provide considerably more reliable convergence to the ground state. © 1997 John Wiley & Sons, Inc. *J Comput Chem* **18**: 1863–1874, 1997

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Introduction

The study of transition-metal-containing systems by *ab initio* quantum chemistry is a challenging and important area of electronic struc-

ture theory. Transition metal systems are difficult to model with empirical force fields or semiempirical methods, necessitating an *ab initio* approach. However, due to the fractional occupation of the *d* shells, a large number of near-degenerate states make electronic structure calculations difficult. Although there has been considerable progress in the application of both wave-function-based methods and density functional theory (DFT) to transition metals over the past decade,^{1–3} there are still both quantitative and qualitative difficulties that are significantly greater than those for organic systems.

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For the past 10 years, we have been developing an *ab initio* electronic structure code, PS-GVB,⁴ utilizing pseudospectral numerical methods to solve Hartree–Fock (HF), DFT, and other correlated electronic structure equations.^{5–13} Indeed, the versatility of the suite of programs has now outgrown the name, originally serving to indicate the novel use of pseudospectral methods (PS) with generalized valence bond (GVB) techniques; now, the PS method is applied to a wide range of theoretical methods. The method employs both a standard Gaussian basis set and a numerical grid to evaluate the great majority of two-electron repulsion integrals, while treating one-electron and large two-electron terms analytically as in standard *ab initio* codes such as Gaussian-92.¹⁴ In applications to a wide range of organic molecules, substantial reductions in CPU time, as compared with Gaussian-92, have been demonstrated for both single-point energy evaluations and geometry optimization, typically on the order of a factor of 3–10 for large systems, with no measurable loss of accuracy as compared with experimental data.^{11,15} In the case of correlated wave-function-based methods, most prominently local MP2 calculations,^{16,17} orders of magnitude reduction in CPU time have been obtained.¹³

Despite these advantages, it is a significant challenge to extend pseudospectral methods to new atoms and basis sets, as one must design suitable numerical grids and fitting bases. A similar difficulty exists in general for DFT calculations, where the level of precision of the calculations is also dependent upon these parameters for most methods of calculation. The only way to be confident about the reliability of any numerical electronic structure method is to carry out tests for a large number of molecules, by comparison with either analytical results or with fully converged numerical results. The first objective of the present study is to present such comparisons for transition-metal-containing species to validate our new pseudospectral implementation of both Hartree–Fock and DFT calculations.

In addition to the robustness of the numerical methods, there are other issues specific to transition metals. One is the convergence of the SCF wave function to the target electronic state (e.g., the ground state). It is well known that construction of a reliable initial guess for a given target state is highly nontrivial for transition metals, and that with existing programs it is often necessary to experiment with modifications of the usual initial

guess to obtain convergence to the desired state. We have developed a new initial guess methodology in which control over the target state is considerably enhanced as compared to alternatives. We demonstrate the performance of this methodology by comparing the ability to converge to the ground electronic state with that of Gaussian-92 using the default initial guess. Second, it is typically desirable to utilize effective core pseudopotentials (ECP) for reasons of both computational efficiency and accuracy (e.g., in more properly addressing relativistic core effects in the metals). We have implemented ECP energies and first derivatives in PS-GVB for several standard transition metal basis sets. Finally, performance of the code with regard to accuracy and computational efficiency must be evaluated. We do this here by explicit comparisons with Gaussian-92 run in its default mode, for a large suite of test cases.

Review of Pseudospectral Methodology

Our pseudospectral methodology has been developed in a series of previous publications. Contracted Gaussian basis functions are employed to represent the molecular orbitals as in conventional electronic structure programs; however, a numerical grid is used in the process of assembling Coulomb and exchange matrix elements by:

$$J_{ij} = \sum_g Q_i(r_g) J(r_g) R_j(r_g) \quad (1)$$

$$K_{ij} = \sum_g Q_i(r_g) K_j(r_g) \quad (2)$$

where $R_j(r_g)$ is the atomic basis function j evaluated at grid point r_g , and $Q_i(r_g)$ is the least-squares fitting operator optimized for the region around basis function i . The physical space operators on the grid are given by:

$$J(r_g) = \sum_{ij} A_{ij}(r_g) \rho_{ij} \quad (3)$$

$$K_i(r_g) = \sum_j A_{ij}(r_g) \sigma_j(r_g) \quad (4)$$

in terms of the one-electron integrals $A_{ij}(r_g) = \int d^3r' \phi_i(r') \phi_j(r') / |r_g - r'|$, the density matrix $\rho_{ij} = \sum_{\alpha} c_{i\alpha} c_{j\alpha}$, and an intermediate quantity $\sigma_j(r_g) = \sum_k R_k(r_g) \rho_{jk}$.

The key to the efficiency of the method is the use of a specially designed least-squares fitting procedure capable of yielding an accurate fit to, for

example, the Coulomb field $J(r_g)$ multiplied by an atomic basis function R_j , but uses a relatively small number of grid points. To this end, local least-squares operators for each atom are defined and the fitting basis is systematically optimized for each of the local operators, as discussed in detail in ref. 10.

To achieve the high accuracy required for *ab initio* electronic structure calculations, it is necessary to supplement the formulations in eq. (1)–(4) by evaluating a small fraction of the two-electron integrals analytically. All one-center and some two- and three-center integrals are computed analytically using standard efficient Gaussian integral methods.^{18,19} Subtracting these terms from the pseudospectral framework to avoid double counting is nontrivial and is discussed in ref. 11.

A final crucial modification of the pseudospectral scheme is the reorganization of eqs. (1) and (2) so that, in the Q_j operator, j is always a “short-ranged” function, meaning that it has Gaussian exponents larger than a threshold cutoff value, typically ~ 0.3 a.u. These Q operators can then be produced with local least-squares fitting, involving a Gaussian weight. The only terms that cannot be so reorganized represent two-electron integrals involving four long-ranged functions. In this case, a global least-squares operator is used in the fitting. However, because only long-range functions are involved in this case, the fitting basis is much smaller and the global least-squares procedure is tractable and accurate.

In our implementation of the pseudospectral methods for transition metals, the formalism described in the aforementioned references, briefly discussed here, is unchanged; the major task is thus the development of grids and fitting basis parameters for the transition metal atoms and ECP basis sets, which is presented in the next section. It is likely that improvements specific to transition metals can be made; such work will be the subject of future publications.

Pseudospectral Parameters

To carry out pseudospectral calculations on new systems, it is necessary to define numerical grids and fitting basis functions corresponding to any as-yet-undefined atoms. Optimization of parameters is carried out by running calculations for a set of test cases and comparing with analytical results. For this purpose, we have selected 25 transition

metal complexes from the Cambridge Data Base²⁰ which will serve as our test suite. Table I provides the archival names for these molecules. A variety of ligands are represented in the complexes, ranging from small ligands, such as CN or Cl^- , to larger cyclopentadienyl (Cp) and ethylenediamine (en) ligands. A variety of charged states are also considered. Finally, each transition metal of interest is represented by at least one complex. The structure of the grid and fitting basis are similar across a given row of the periodic table, with the actual values of the parameters (the grid radii, and the fitting function Gaussian exponents) being modified to reflect the specific electronic structure of the atom.

Parameter sets have been developed for two basis sets for two popular effective core potential

TABLE I. Molecules in the Test Suite for this Study Along with Their Cambridge Data Base Designations.

Formula	CDB Name
ScCp ₂ Me	FEDSUC ^a
Ti(tol) ₂	BITRUR10
VCp ₂	CPNDYV02
Cr(CO) ₆	FOHCOU
Mn(H ₂ O) ₆ ²⁺	COLWUV
Fe(H ₂ O) ₆ ³⁺	CEYRIH
Co(NH ₃) ₆ ³⁺	DAJWAM
Ni(CN) ₄ ²⁻	CARRES
Ni(H ₂ O) ₆ ²⁺	FEGLUY
Cu(H ₂ O) ₆ ²⁺	JADPEJ
Zn(H ₂ O) ₆ ²⁺	CAXYUV
Y(H ₂ O) ₉ ³⁺	AYETHS01
Zr(CO) ₆ ²⁻	SIDGOB
ZrCp ₂ (CO) ₂	CCPZRA ^b
ZrCp ₂ (C ₂ H ₄)Me ⁺	
Nb(CO) ₆ ⁻	BILNEP10 ^c
NbCp ₂ Cl ₂ ⁺	SIGXEL
Mo(CO) ₆	FUBYIK
Tc(NCS) ₆ ³⁻	BAICTC
RuCp ₂	CYCPRU06
Rh(en) ₂ Cl ₂ ⁺	CENRHB01
Pd(CN) ₄ ²⁻	EATCPD
Pd(NH ₃) ₄ ²⁺	APDPZC
AgPy ₄ ⁺	BADTEF10
Cd(en) ₂ ²⁺	DANKEI

^aDerived from CDB reference FEDSUC, but with the Cp* ligands replaced by Cp groups.

^bA larger zirconium complex included to contrast the performance of the calculations with respect to the smaller zirconium complexes.

^cNb(CO)₆⁻ fragment taken from the *bis*-(PPh₃)-iminium / Nb(CO)₆⁻ complex.

(ECP) basis sets, the Los Alamos LAV3P^{21,22} and LACVP²³ sets. Once parameters have been developed for a given atom, extensions to additional basis sets are typically straightforward. However, implementation for all-electron basis sets will require additional work.

NUMERICAL GRIDS

The radial grids we use for titanium, a representative first-row transition metal, and zirconium, a representative second-row metal, are presented in Table II. The generation of these grids is done in the same manner as in previous publications⁸—grid points are atom-centered and distributed in radial shells to exactly integrate spherical harmonics up to a certain order in each shell. Atomic grids are fused into a molecular grid via truncation at Voronoi surfaces.

Only one grid density, designated the “fine” grid, is used on the transition metal in our calculations, whereas for the other atoms, a less dense “medium” grid is used on most of the iterations; this multigrid strategy is more completely explained in ref. 9 and 11. For calculations on

organometallic systems, development of a medium grid is unnecessary because the number of transition metal atoms is very small, in most cases one. It is important to emphasize here that pseudospectral grids are far less dense than those typically used for DFT calculations, which require thousands of points per atom. We are able to use far fewer points because of the specially optimized nature of the least-squares fitting procedure.

FITTING BASIS

Table III presents the fitting basis parameters we use for titanium and zirconium for the LACVP** basis set. The fitting basis is composed of the normal Gaussian basis set functions, as well as additional functions, called dealiasing functions in the Fourier transform literature,^{24,25} which serve to filter out the error in fitting onto a finite basis. Each atomic-based *Q* least-squares operator is constructed from the fitting basis functions of that atom, as well as some of the short-ranged fitting functions of surrounding atoms. The table illustrates the contributions each atom will contribute to its first, second, and third-shell neighbors. The left-over long-range fitting functions, used for fully long-ranged integrals are collected in the global *Q* operator as indicated in the table.

The size of the atomic-based fitting matrices of the pseudospectral method is kept to a minimum by enforcing the exclusion of distant functions through a multiplicative envelope function, $\exp(-\lambda r^2)$, which weights gridpoints according to their proximity to the atomic center; λ is the smallest radial exponent in the valence atomic basis set. This is more fully described in ref. 10. The special connectivity circumstances in transition-metal complexes, where often the central metal had four to eight ligand atoms, have caused us to make two modifications to this scheme to minimize pseudospectral error, thereby promoting efficient SCF convergence. First, for metals with a large default falloff exponent (e.g., the 0.876 exponent for Ni in the LACVP** basis), we have reset this value to a fixed value 0.55. In addition, for cases with many (> 4) carbon atoms bonded to the metal, we have halved the envelope function (coming from 2*sp* exponent of 0.544) for those centers. The net effect of these modifications is to broaden the range for which the least-squares matrix will be most accurately fit against—enclosing more of the multiconnected volume around the transition metal. Our experimentation has shown it to be unnecessary to perform this procedure for other neighbor ligand

TABLE II. Sample Grid Parameters for Transition Metals.^a

Fine Grid					
Titanium			Zirconium		
Shell	Radius (a ₀)	# Points	Shell	Radius (a ₀)	# Points
1	0.53217	6	1	0.64997	6
2	0.74027	8	2	0.88851	8
3	0.92764	12	3	1.09717	12
4	1.21112	24	4	1.40173	24
5	1.72706	38	5	1.93119	38
6	2.45332	60	6	2.65453	60
7	3.77782	110	7	3.86247	110
8	5.78986	110	8	5.72920	110
9	8.10048	60	9	7.61451	60
10	12.06492	38	10	10.63941	38
11	16.12589	24	11	13.82528	24
12	20.02021	12	12	16.92531	12
13	23.92602	8	13	20.05569	8
14	30.82853	6	14	25.17328	6

^a Titanium and zirconium are shown as representative of their respective rows of the periodic table. Only one grid density is used for the metal, whereas, for main-group elements, different densities are used during the SCF iterative process.

TABLE III.
Sample Transition Metal Gaussian Fitting Functions.^a

Exponent	Long-Range	Atom	Neighbor	Next-nbr.	NN-nbr.
Titanium					
0.008791	<i>spd</i>	—	—	—	—
0.016000	<i>spd</i>	<i>spd</i>	<i>spd</i>	<i>sp</i>	<i>sp</i>
0.029120	<i>pd</i>	—	—	<i>p</i>	—
0.031400	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—
0.053000	<i>spd</i>	<i>spdf</i>	<i>spdf</i>	<i>spd</i>	—
0.087200	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—
0.115700	—	<i>d</i>	<i>d</i>	<i>d</i>	—
0.175562	<i>spd</i>	<i>spd</i>	<i>spd</i>	<i>sp</i>	—
0.581551	<i>spd</i>	<i>sp</i>	<i>sp</i>	—	—
(3 <i>s</i>)	—	<i>s</i>	<i>s</i>	<i>s</i>	—
(4 <i>s</i>)	—	<i>s</i>	<i>s</i>	<i>s</i>	—
(3 <i>p</i>)	—	<i>p</i>	<i>p</i>	<i>p</i>	—
(3 <i>d</i>)	—	<i>d</i>	<i>d</i>	<i>d</i>	—
Zirconium					
0.014078	<i>spd</i>	—	—	—	—
0.024300	<i>spd</i>	<i>spd</i>	<i>spd</i>	<i>sp</i>	<i>sp</i>
0.033400	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—
0.041944	<i>pd</i>	—	—	<i>p</i>	—
0.072400	<i>sp</i>	<i>sp^f</i>	<i>sp^f</i>	<i>sp</i>	—
0.080200	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	—
0.100100	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—
0.215710	<i>sp</i>	<i>sp</i>	<i>sp</i>	<i>sp</i>	—
0.642692	<i>spd</i>	<i>sp</i>	<i>sp</i>	—	—
(4 <i>s</i>)	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	—
(5 <i>s</i>)	—	<i>s</i>	<i>s</i>	<i>s</i>	—
(4 <i>p</i>)	<i>p</i>	<i>p</i>	<i>p</i>	<i>p</i>	—
(4 <i>d</i>)	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	—

^a Titanium and zirconium are representative of their respective rows of the periodic table. The valence basis functions are indicated in bold; the other entries constitute the augmented "dealiasing" functions of the fitting set. Orbital symbols represent the inclusion of the entire contracted basis function.

atoms; however, we do not yet know if this is exhaustively true; we reserve a more complete discussion of this for a subsequent work.

The fitting basis is considerably larger than the original basis. However, the construction of the least-squares matrices is done in a preprocessing step prior to the SCF calculation, and the operators are reused throughout the iterative process. The contribution of the least-squares procedure to the CPU time is typically less than 10% for large molecules.

Initial Guess and SCF Improvements

It is well known that it is difficult to generate a good set of initial orbitals for *ab initio* calculations

involving transition metals. The semiempirical methods that have been used so successfully for generating initial guesses in organic systems have been less than reliable for systems involving transition metals. We believe that, unless semiempirical techniques are able to properly include the special chemistry of *d* orbitals, they will always fail in delivering reasonable parameterizations.

For the moment, we have abandoned the semiempirical approach in favor of a simpler scheme based on the overlap between the valence orbitals. The idea is simply to find the best set of linear combinations of the valence orbitals with the maximum amount of bonding character. We already have employed such a scheme successfully for organic systems,²⁶ and the present article demonstrates that the same approach can also be used successfully for inorganic systems.

The first step in our approach is to select a set of atomic valence orbitals. A unique set of such orbitals can be obtained by performing HF-SCF calculations for each atomic basis independently. Typically, the results of the atomic calculations are saved to disk, saving the need to redo the atomic HF-SCF calculations for each new molecule. At this point, the atomic valence orbitals have zero intraatomic overlap but nonzero interatomic overlap; they are also occupation-averaged, because orbitals of the same symmetry are treated as equivalent. The best bonding set of the linear combinations of the atomic valence orbitals is obtained by diagonalizing the matrix of overlaps between the atomic valence orbitals. The eigenvectors with the largest eigenvalues have the highest bonding character. The mathematical details are identical to those described in Section 3 of ref. 26 and are not repeated here. The only modification to the ap-

proach we have made in this work, in order to favor bonding for orbitals with lower energies, is to add $-\alpha E_{\text{orbital}}$ to the diagonal elements of the overlap matrix, where E_{orbital} is the valence orbital energy obtained from the atomic SCF calculations, and α is an empirical parameter set to 0.1.

Results

SINGLE-POINT CALCULATIONS

All comparisons are made with the Gaussian-92 *ab initio* electronic structure package and both programs were run in direct mode. Whereas other programs may be superior in performance to Gaussian-92 for transition metal systems in some respects, although not in computation time to our knowledge, it is still the case that the overwhelming majority of users employ the Gaussian series of

TABLE IV. Comparison of Performance at the HF Level with the LACVP** Basis Set on an IBMS P / 2 Thin Node.^a

Molecule	Gaussian-92				PS-GVB				Basis Functions	CPU Ratio
	Energy (a.u.)	It.	CPU	CPU / It.	Energy (a.u.)	It.	CPU	CPU / It.		
ScCp ₂ Me	-470.04209	15	8701.9	643.8	-470.04225	8	2693.8	288.8	241	3.23
Ti(tol) ₂	-596.72909	25	29027.4	1157.1	-596.80789	8	4534.0	500.0	298	6.40
VCp ₂	-455.13596	16	4743.4	598.5	-455.10070	9	2627.7	270.2	212	1.81
Cr(CO) ₆	-761.95019	13	1715.0	129.5	-761.95048	12	1351.5	115.8	190	1.27
Mn(H ₂ O) ₆ ²⁺	-558.72563	22	1948.1	87.4	-558.72788	11	1482.9	128.3	166	1.31
Fe(H ₂ O) ₆ ³⁺	-576.50471	14	1223.1	85.6	-576.50661	12	677.4	53.1	166	1.81
Co(NH ₃) ₆ ³⁺	-479.94221	11	1786.8	175.1	-479.94190	11	1083.8	88.2	196	1.65
Ni(CN) ₄ ²⁻	-537.48650	12	485.1	39.1	-537.48686	11	529.5	44.7	134	0.92
Ni(H ₂ O) ₆ ²⁺	-623.37696	20	1495.6	79.0	-623.37862	8	481.2	51.7	166	3.11
Cu(H ₂ O) ₆ ²⁺	-650.04342	27	2442.5	88.8	-650.06881	7	953.0	129.0	166	2.56
Zn(H ₂ O) ₆ ²⁺	-518.62090	7	448.9	59.9	-518.62118	7	395.0	46.9	163	1.14
Y(H ₂ O) ₉ ³⁺	-721.19324	7	1302.6	177.5	-721.19278	7	1270.0	152.2	238	1.03
Zr(CO) ₆ ²⁻	-722.34603	11	989.2	88.6	-722.34630	8	573.5	63.8	190	1.73
ZrCp ₂ (CO) ₂	-655.98274	13	5020.4	380.5	-655.98293	9	2037.4	198.0	268	2.46
ZrCp ₂ (C ₂ H ₄)Me ⁺	-548.08240	14	12722.4	999.5	-548.08206	8	3859.6	431.9	304	3.30
Nb(CO) ₆ ⁻	-732.20816	9	841.9	90.0	-732.20842	9	628.8	62.9	190	1.34
NbCp ₂ Cl ₂ ⁺	-1358.61602	10	2023.3	197.9	-1358.61640	9	1097.5	104.0	248	1.84
Mo(CO) ₆	-743.36962	9	954.6	111.9	-743.36955	9	745.0	73.2	190	1.28
Tc(NCS) ₆ ³⁻	-3018.35864	15	7419.6	487.6	-3018.35874	19	7376.0	375.0	298	1.01
RuCp ₂	-477.59261	10	2383.1	243.1	-477.59253	8	1190.1	123.9	212	2.00
Rh(en) ₂ Cl ₂ ⁺	-1405.37677	11	3477.6	309.9	-1405.37753	8	1485.1	165.5	250	2.34
Pd(CN) ₄ ²⁻	-495.14620	9	708.6	76.0	-495.14665	8	272.1	29.8	134	2.60
Pd(NH ₃) ₄ ²⁺	-350.05357	8	393.4	46.1	-350.05330	7	322.3	36.7	138	1.22
AgPy ₄ ⁺	-1131.48146	8	4013.5	469.8	-1131.48167	9	2549.4	261.0	458	1.57
Cd(en) ₃ ²⁺	-613.63044	6	4719.4	839.9	-613.63049	7	3480.4	447.5	307	1.36

^a Bold entries indicate excited states obtained: 5 of 25 cases for Gaussian-92, 1 of 25 for PS-GVB. It.: number of SCF iterations; CPU: user CPU seconds for total calculation; CPU / It.: average CPU seconds per iteration; CPU ratio: factor of total CPU times.

programs for their calculations. Our principle objective here in any case is to have some way of evaluating the performance we have achieved with PS-GVB in terms of both speed and accuracy.

The first issue to be considered is convergence of the HF or BLYP^{27–29} and B3LYP^{27–30} DFT procedures to the appropriate electronic state. For present purposes, we wish to converge all molecules to the ground, low-spin electronic state. In cases where PS-GVB and Gaussian-92 disagree significantly in energy, we have distinguished between errors in PS-GVB and genuinely obtaining different electronic states by taking the PS-GVB wave functions and inserting them into Gaussian-92 and vice versa. The boldface entries in Tables IV–VII indicate that this procedure yielded an excited state. It can be seen that PS-GVB converges very infrequently to an excited state, whereas Gaussian-92 converges to an excited state in 20–25% of all cases, largely in the first-row series,

which are usually the most difficult to treat due to the large size difference between the ligand *s* orbitals and the metal *d* shell.³ The difference in performance is primarily attributable to the difference in the initial guess methods, as discussed in the previous section.

Eliminating cases where Gaussian-92 converges to an excited state, we next consider the accuracy of the PS-GVB total energies, examining the HF results for both basis sets. (Because Gaussian-92 uses a numerical grid in its DFT calculations, these comparisons would be less clear with regard to any discrepancies.) The great majority of molecules display agreement to better than 0.25 kcal/mol in total energy, comparable to the results we have obtained for organic molecules. There are a few cases where the discrepancy is larger, on the order of 0.3–0.4 kcal/mol. This reflects the greater total energy of transition-metal-containing system, and the smaller amount of effort to date which has

TABLE V. Comparison of Performance at the HF Level with the LAV3P** Basis Set on an IBM SP / 2 Thin Node.^a

Molecule	Gaussian-92				PS-GVB				Basis Functions	CPU Ratio
	Energy (a.u.)	It.	CPU	CPU / It.	Energy (a.u.)	It.	CPU	CPU / It.		
ScCp ₂ Me	–425.60894	9	4801.9	585.0	–425.60896	8	2420.6	257.6	238	1.98
Ti(tol) ₂	–542.64631	11	11892.1	1070.5	–542.64606	8	4223.2	462.5	298	2.82
VCp ₂	–390.56352	17	3960.0	230.4	–390.56358	37	9099.8	240.7	212	0.44
Cr(CO) ₆	–686.33212	10	1184.4	115.1	–686.33241	12	996.8	76.1	187	1.19
Mn(H ₂ O) ₆ ²⁺	– 470.19858	61	4100.6	66.8	–470.63792	18	2022.5	108.6	166	2.03
Fe(H ₂ O) ₆ ³⁺	– 467.89094	65	6500.2	99.9	–475.39678	12	577.6	45.0	166	11.25
Co(NH ₃) ₆ ³⁺	– 360.39881	59	8063.0	136.0	–365.22093	8	728.9	77.7	196	11.06
Ni(CN) ₄ ^{2–}	– 408.23478	20	701.1	34.1	–408.23550	12	579.3	45.2	134	1.21
Ni(H ₂ O) ₆ ²⁺	– 494.13725	16	1084.4	66.1	–494.13879	7	401.5	47.8	163	2.70
Cu(H ₂ O) ₆ ²⁺	– 505.17961	17	1353.2	77.9	–505.50862	7	853.6	114.9	163	1.58
Zn(H ₂ O) ₆ ²⁺	–518.62090	7	450.4	60.2	–518.62118	7	385.9	46.2	163	1.17
Y(H ₂ O) ₉ ³⁺	–685.06705	7	1163.4	157.0	–685.06659	7	1046.3	128.0	238	1.11
Zr(CO) ₆ ^{2–}	–679.09942	10	793.8	76.1	–679.09945	8	493.4	56.2	187	1.61
ZrCp ₂ (CO) ₂	–612.73161	9	3307.0	358.8	–612.73120	9	1812.3	179.7	268	1.82
ZrCp ₂ (C ₂ H ₄)Me ⁺	–504.81474	9	7575.1	827.1	– 504.81320	8	3508.8	397.7	304	2.16
Nb(CO) ₆ [–]	–681.42269	8	731.5	87.2	–681.42273	10	653.4	59.4	190	1.12
NpCp ₂ Cl ₂ ⁺	–418.27644	10	1432.9	136.8	–418.57689	9	851.9	76.7	227	1.68
Mo(CO) ₆	–684.34527	9	845.2	90.0	–684.34561	9	646.9	64.2	187	1.31
Tc(NCS) ₆ ^{3–}	– 624.90235	15	4972.6	315.0	–624.90691	11	2907.1	24.7	298	1.71
RuCp ₂	–400.84581	12	2376.1	193.8	–400.84507	8	1082.7	112.6	212	2.19
Rh(en) ₂ Cl ₂ ⁺	–429.34897	12	2742.7	220.2	–429.34953	8	1181.6	125.6	250	2.32
Pd(CN) ₄ ^{2–}	–398.43795	8	552.9	66.1	–398.43797	8	237.1	25.8	134	2.33
Pd(NH ₃) ₄ ²⁺	–253.34287	8	343.3	39.9	–253.34276	7	285.0	32.0	138	1.20
AgPy ₄ ⁺	–1024.00423	8	3916.0	459.1	–1024.00441	9	2484.2	254.8	458	1.58
Cd(en) ₃ ²⁺	–613.63044	6	4642.4	749.9	–613.63049	7	3456.5	443.8	307	1.34

^a Bold entries indicate excited states obtained: 7 of 25 cases for Gaussian-92, 1 of 25 for PS-GVB. It.: number of SCF iterations; CPU: user CPU seconds for total calculation; CPU / It.: average CPU seconds per iteration; CPU ratio: factor of total CPU times.

TABLE VI.
Comparison of Performance with the BLYP DFT Method Using the LACVP Basis Set on an IBM SP / 2 Thin node.^a**

Molecule	Gaussian-92				PS-GVB				Basis Functions	CPU Ratio
	Energy (a.u.)	It.	CPU	CPU / It.	Energy (a.u.)	It.	CPU	CPU / It.		
ScCp ₂ Me	-473.08596	18	14615.0	808.0	-473.08574	9	4897.7	489.6	241	2.98
Ti(tol) ₂	-600.75800	27	43482.8	1469.4	-600.75613	10	10281.9	952.7	298	4.23
Cr(CO) ₆	-766.26145	59	9767.0	165.0	-766.26190	12	1952.4	154.4	190	5.00
Mn(H ₂ O) ₆ ²⁺	-551.24552	12	1742.0	142.6	-561.66408	14	4210.4	293.9	166	0.41
Co(NH ₃) ₆ ³⁺	-481.71278	8	2150.3	264.3	-482.81371	9	1726.4	173.1	196	1.25
Ni(CN) ₄ ²⁻	-540.62934	19	1078.0	55.8	-540.62963	10	539.6	50.2	134	2.00
Ni(H ₂ O) ₆ ²⁺	-626.44910	56	6986.0	124.3	-626.46058	9	974.6	97.9	166	7.17
Cu(H ₂ O) ₆ ²⁺	-653.19524	13	2059.8	156.1	-653.19541	24	6066.9	249.7	166	0.34
Zn(H ₂ O) ₆ ²⁺	-523.12522	10	1150.2	111.4	-523.12559	8	790.2	87.8	163	1.46
Y(H ₂ O) ₉ ³⁺	-724.87011	9	2843.0	309.0	-724.86953	7	2056.8	254.6	238	1.38
Zr(CO) ₆ ²⁻	-726.42910	15	2007.9	131.7	-726.42957	12	1434.6	113.7	190	1.40
ZrCp ₂ (CO) ₂	-659.96770	16	8474.4	524.9	-659.96736	12	4135.5	319.1	268	2.05
ZrCp ₂ (C ₂ H ₄)Me ⁺	-551.69112	18	23074.0	1275.0	-551.69069	9	6991.7	706.5	304	3.30
Nb(CO) ₆ ⁻	-736.32142	11	1573.0	140.0	-736.32140	11	1207.6	103.4	190	1.30
NbCp ₂ Cl ₂ ⁺	-1362.92679	13	3413.8	258.3	-1362.92689	11	1999.9	165.3	248	1.71
Mo(CO) ₆	-747.47947	12	1828.2	149.4	-747.47931	9	1204.4	123.2	190	1.52
RuCp ₂	-480.72819	14	4303.5	303.4	-480.72529	10	2561.5	233.7	212	1.68
Rh(en) ₂ Cl ₂ ⁺	-1409.74030	12	5534.4	455.2	-1409.74127	12	3607.1	281.2	250	1.53
Pd(CN) ₄ ²⁻	-498.02060	13	1406.3	106.4	-498.02109	10	588.5	55.3	134	2.39
Pd(NH ₃) ₄ ²⁺	-352.10692	11	972.4	86.1	-352.10690	7	578.5	70.8	138	1.68
AgPy ₄ ⁺	-1138.10277	14	10330.8	719.0	-1138.10295	9	3934.7	396.8	458	2.63
Tc(NCS) ₆ ³⁻	-3026.06855	24	19629.3	813.3	-3026.08319	15	12501.4	813.0	298	1.57
Cd(en) ₃ ²⁺	-618.62725	8	10038.4	1235.7	-618.62754	8	6861.9	768.4	307	1.46

^a Bold entries indicate excited states obtained: 5 of 23 cases for Gaussian-92, 2 of 23 for PS-GVB. VCp₂ and Fe(H₂O)₈³⁺ did not converge with either program. It.: number of SCF iterations; CPU: user CPU seconds for total calculation; CPU / It.: average CPU seconds per iteration; CPU ratio: factor of total CPU times.

been put into grid and dealiasing function optimization. However, quantum chemical results for transition metal systems are in any case less accurate compared to experiment than those for organic molecules. Additionally, we have typically found that pseudospectral “errors” cancel for quantities such as conformational energy, just as basis set errors do. For the present, we consider this level of accuracy to be adequate.

We next examine the computational efficiency of PS-GVB and Gaussian-92 for single-point energy calculations. Both programs were run with default cutoffs, which mandate an energy convergence to 5×10^{-5} hartree. The molecules studied here are relatively small in size; the largest calculations are on the order of 300 basis functions. However, a two- to threefold speedup factor is observed for PS-GVB for many of the larger systems; for example, those containing two Cp rings. Note that group IIB elements (Zn, Cd) have the same basis functions in the LACVP** and LAV3P** bases; there-

fore, different timings for such complexes in Tables IV and V merely indicate normal variations in computer throughput. Comparable speedups are obtained for DFT and HF calculations on the same basis set, in almost all cases, although we note the few cases where PS-GVB performed slower; we believe that these cases will be better treated through improved grids and fitting functions as well as ongoing optimizations in our DFT code. The overall scaling behavior of the two programs is manifested in examining the three zirconium complexes: Zr(CO)₆²⁻, ZrCp₂(CO)₂, and ZrCp₂(C₂H₄)Me⁺. At the HF/LACVP** level, for example, PS-GVB is 1.7 times faster than Gaussian-92 for the 190-basis-function hexacarbonyl complex. This factor increases to over 3 for the latter structure using 304 basis functions.

The above discussion is based on the final columns in Tables IV–VII; that is, of the overall throughput of the two approaches. To distinguish the differences in iteration schemes we also tabu-

TABLE VII.
Comparison of Performance with the B3LYP DFT Method Using the LACVP Basis Set on an IBM SP / 2 Thin node.^a**

Molecule	Gaussian-92				PS-GVB				Basis Functions	CPU Ratio
	Energy (a.u.)	It.	CPU	CPU / It.	Energy (a.u.)	It.	CPU	CPU / It.		
ScCp ₂ Me	-473.38402	16	15043.6	935.8	-473.38374	9	4942.4	494.0	240	3.04
Ti(tol) ₂	- 589.92638^b	> 37	> 18h	(1750)	-601.09919	10	9324.4	857.3	298	> 7.0
VCp ₂	- 445.35943	65	24768.1	380.8	-458.36761	15	9923.3	646.2	212	2.50
Cr(CO) ₆	-766.36233	24	4539.6	187.9	-766.36282	14	2347.8	160.7	190	1.93
Mn(H ₂ O) ₆ ²⁺	- 561.82520	38	6343.8	166.1	-561.82834	15	3257.5	210.6	166	1.95
Co(NH ₃) ₆ ³⁺	-483.03833	19	5410.7	282.9	-483.03768	8	1500.0	166.4	196	3.61
Ni(CN) ₄ ²⁻	-540.74674	14	901.0	63.1	-540.74707	9	490.1	49.9	134	1.84
Ni(H ₂ O) ₆ ²⁺	- 626.66018	12	1707.0	140.1	-626.66226	8	900.0	100.8	166	1.90
Cu(H ₂ O) ₆ ²⁺	-653.40875	16	3048.7	188.6	-653.40898	9	2162.1	231.9	166	1.41
Zn(H ₂ O) ₆ ²⁺	-522.95554	10	1294.3	126.4	-522.95588	7	680.4	24.8	163	1.90
Y(H ₂ O) ₉ ⁺	-725.11284	7	2587.2	360.7	-725.11228	7	2069.5	255.4	238	1.25
Zr(CO) ₆ ²⁻	-726.56063	13	1907.8	144.2	-726.56106	9	963.7	99.4	190	1.98
ZrCp ₂ (CO) ₂	-660.26801	14	8617.6	610.1	-660.26779	9	3278.4	329.3	268	2.63
ZrCp ₂ (C ₂ H ₄)Me ⁺	-552.02417	14	21002.5	1491.3	-552.02385	9	6947.5	702.2	304	3.02
Nb(CO) ₆	-736.45491	10	1577.4	154.4	-736.45483	8	911.4	105.1	190	1.73
NbCp ₂ Cl ₂ ⁺	-1363.22313	13	3843.2	291.4	-1363.22332	11	2351.3	197.1	248	1.63
Mo(CO) ₆	-747.61944	10	1734.0	169.9	-747.61931	9	1227.3	125.4	190	1.41
Tc(NCS) ₆ ³⁻	- 3026.36973	32	26195.0	815.1	-3026.37432	13	10878.9	813.8	298	2.41
RuCp ₂	-480.99500	13	4434.9	337.2	- 480.99252	8	2120.4	236.0	212	2.09
Rh(en) ₂ Cl ₂ ⁺	-1410.08402	10	5234.1	516.2	-1410.08485	8	2568.7	291.8	250	2.04
Pd(CN) ₄ ²⁻	-498.19198	12	1451.3	118.9	-498.19249	9	487.5	50.3	134	2.98
Pd(NH ₃) ₄ ²⁺	-352.31888	11	1078.2	95.8	-352.31885	7	579.5	70.9	138	1.86
AgPy ₄ ⁺	-1138.65700	13	18685.8	1417.0	-1138.65721	8	3536.8	396.9	458	5.28
Cd(en) ₃ ²⁺	-618.76853	7	10204.5	1435.9	-618.76881	7	6272.9	794.1	307	1.63

^a Bold entries indicate excited states obtained: 5 of 24 cases for Gaussian-92, 1 of 24 for PS-GVB. It.: number of SCF iterations; CPU: total user CPU seconds; CPU / It.: average CPU seconds per iteration; CPU ratio: factor of total CPU times.

^b Job exceeded the 18-hour wall clock limit at CTC. Fe(H₃O)₆³⁺ did not converge with either program.

late the average CPU time per SCF iteration in the two programs, and these columns indicate the raw performance of the integral evaluation and matrix manipulation operations. Here also, the pseudospectral approach regularly exhibits a twofold improvement in many cases. In sum, not only is PS-GVB performing the raw, per iteration calculations faster, but it is frequently converging in fewer SCF cycles, and these cumulative effects yield the overall pseudospectral timing improvement over conventional methods.

We note that Hartree-Fock calculations are inadequate to describe quantitatively ligand-metal dissociation and electronic spectroscopy.³¹ They also have difficulties in open-shell transition metal complexes, where including electron correlation would help compensate for HF's strong favoritism for high multiplicity states.³² In this light, we view the present work as a building block for our ongoing

studies incorporating correlation via generalized valence bond³³ or local Møller-Plesset^{13,34} perturbation techniques.

GEOMETRY OPTIMIZATIONS

Whereas Hartree-Fock methods have difficulty describing much of the chemistry in transition metals, their performance in geometry optimization is quite adequate, as the correlation energy is relatively constant over the conformational space of the molecule being optimized.³ Comparing results for geometry optimization is somewhat more difficult than for single-point calculations, as one must sort out the performance of the geometry optimizer from the CPU time per iteration. We have attempted to do this in Tables VIII and IX, although the results are not entirely satisfactory because of various problems we encountered in

running Gaussian-92. These difficulties should not necessarily be taken as reflective of the performance of that program in the hands of an expert, as we did not put an enormous amount of effort into making recalcitrant cases perform property. In addition, efforts to match cases where PS-GVB and Gaussian-92 use the same molecular symmetry proved to be difficult, because PS-GVB is capable of working with non-Abelian groups, whereas Gaussian-92 is not; this is another significant advantage of PS-GVB, on top of the algorithmic scaling. A number of jobs with no (C_1) symmetry are also shown in Table VIII; these results remove symmetry as a factor controlling performance.

Despite the technical difficulties, some general conclusions can be drawn from the results. First, the geometry optimizer of PS-GVB performs at least as well as that in Gaussian-92 with regard to robustness and rapidity of convergence. Second, the advantage in CPU time per iteration is larger for geometry optimization, typically between a factor of three to five, than for single-point calculations, where the speedup is a factor of two to three. Finally, the superior performance of PS-GVB for SCF convergence is manifested in this comparison as well, as the quadratic convergence option in Gaussian-92 had to be used in some cases to obtain ground-state results. The lone structural outlier in Table IX is that of $\text{NbCp}_2\text{Cl}_2^+$ run without symme-

try, where PS-GVB maintained the eclipsed conformation of the Cp rings, while Gaussian-92 attempted to reach a staggered geometry, but did not finish this task in the maximum number of iterations allowed for this job. This phenomenon has been noted in other structures we have optimized with both programs, and does not constitute a failure of either of them, but simply reflects two different minima achieved with different optimization schemes.

The algorithmic and performance improvements of our geometry optimization programs merit a more complete discussion than presented here, and a comprehensive study with this purpose is in preparation.

Conclusions

To summarize, the PS-GVB program appears to provide robust performance for transition metal systems, in terms of energies, SCF convergence, and geometry optimization. The computational efficiency and reliability have been shown to be superior, as compared with Gaussian-92, for a wide range of transition metal complexes and two widely used basis sets employing effective core potentials. For larger systems, we expect that the performance differential will be increased substan-

TABLE VIII.
HF Geometry Optimization Results Using the LACVP** Basis Set.

Molecule	Gaussian-92				PS-GVB				Basis Functions	CPU / It. Ratio
	Symm.	Iter.	CPU (s)	CPU / It.	Symm.	Iter.	CPU (s)	CPU / It.		
Nb(CO) ₆ ⁻	C ₁	2 ^a	5471.1	2735.6	C ₁	106	(108188) ^e	990.3	190	(2.76)
Ti(tol) ₂	C ₁	25 ^b	562855.8	22514.2	C ₁	25	103465.3	4138.6	298	(5.44)
Ni(CN) ₄ ²⁻	D ₂	5 ^c	10319.8	2064.4	D _{4h}	6	953.1	158.9	134	11.0
Ni(CN) ₄ ²⁻	C ₁	2 ^a	2910.0	1455.0	C ₁	18	7452.0	414.0	134	(3.51)
RuCp ₂	C _{2v}	7	8437.8	1205.4	D _{5h}	7	2231.2	319.7	212	3.77
RuCp ₂	C ₁	22	166011.0	7545.9	C ₁	14	23848.5	1703.5	212	4.43
Pd(CN) ₄ ²⁻	D ₂	5	1712.5	342.5	D _{4h}	4	628.4	157.1	134	2.18
Pd(CN) ₄ ²⁻	C ₁	2 ^a	1476.2	738.1	C ₁	11	5031.8	457.4	134	(1.61)
NbCp ₂ Cl ₂ ⁺	C _{2v}	26	91421.5	3516.2	C _{2v}	10	11110.3	1111.0	248	3.16
NbCp ₂ Cl ₂ ⁺	C ₁	73 ^d	675613.4	9255.0	C ₁	18	53177.9	2954.3	248	3.13

Timings are thin-node IBM / 2 times.
^a Geometry not fully optimized because geometry angle was out of range error.
^b Geometry not fully optimized because consistency error in file IO was encountered.
^c Quadratic convergence (SCF = QC) required.
^d Reached maximum number of optimization cycles.
^e Time is sum of an initial and restarted job; the job was interrupted by a computer reboot.

TABLE IX.
Structural Comparison of Converged Jobs of Table VIII.^a

Molecule	Symmetry	G92 energy	PS energy	RMS(<i>r</i>)	RMS(<i>θ</i>)	RMS(<i>ω</i>)	RMSd
Ni(CN) ₄ ²⁻	Yes	-537.51561	-537.51596	0.0053	—	—	0.0051
RuCp ₂	Yes	-477.60912	-477.60872	0.0012	0.0246	—	0.0020
RuCp ₂	No	-477.60911	-477.60879	0.0004	0.0684	0.1115	0.0045
Pd(CN) ₄ ²⁻	Yes	-495.16095	-495.16128	0.0048	—	—	0.0045
NbCp ₂ Cl ₂ ⁺	Yes	-1359.07237	-1359.07192	0.0017	0.1506	0.1055	0.0072
NbCp ₂ Cl ₂ ⁺	No	(-1359.07256)	-1359.07188	0.0042	1.5296	5.5367	0.3435

^a Symmetry column differentiates structures run with symmetry or without. RMS values are averages over the type of internal coordinate: bond lengths, angles, and proper torsions, and a dash indicates that variables of that type are fixed due to symmetry. RMSd is a total structural deviation between atomic coordinates. The final case reflects the fact that different physical minimum structures were reached with the two programs.

tially, as has been observed with organic molecules, particularly for geometry optimization. Work to enhance the grids and dealiasing functions for these and other transition metal systems continues, and work studying such systems as presented here with correlation methods is in progress.

Appendix

A full set of parameters, encompassing all the transition metals addressed in this work, along with molecular structures, are available from the authors upon request.

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